

**ELECTRON MICROSCOPY TECHNIQUE FOR DETERMINATION OF
DISPERSOID DISTRIBUTION IN POWDER BLENDS**

By Bruno C. Buzek

Lewis Research Center
Cleveland, Ohio

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

For sale by the Clearinghouse for Federal Scientific and Technical Information
Springfield, Virginia 22151 - CFSTI price \$3.00

ELECTRON MICROSCOPY TECHNIQUE FOR DETERMINATION OF DISPERSOID DISTRIBUTION IN POWDER BLENDS

by Bruno C. Buzek

Lewis Research Center

SUMMARY

The ability to clearly observe and distinguish between oxide and metal particles in a starting powder blend and to determine the initial distribution of the oxide prior to consolidation enables predictions to be made about the final distribution of the oxide particles in a fully consolidated product. A new electron-microscope specimen-preparation technique was developed to aid in making these predictions. This procedure makes it possible to ascertain the size and the degree of agglomeration of the oxide particles, unobstructed by the presence of the metal-matrix particles, before the compaction and sintering of the powder blend. In the application of this technique, the initial powder blend is enveloped with a thin layer of carbon, and the metal phase is leached out. The retained particles then reveal the state of the dispersoid phase after the blending operation. Nickel, tungsten, chromium, and nichrome, each blended with thoria or alumina, were investigated with the use of this technique. A good correlation exists between the dispersoid distribution in the initial blend and the state of agglomeration in the final sintered product; that is, if small oxide particles were well distributed in the initial powder blend, they remained in a similar state in the final product. On the other hand, if the small oxide particles were clustered in the original powder blend, they appeared as large particles similar in size to the initial clusters after consolidation.

INTRODUCTION

The mechanical blending method of producing dispersion-strengthened materials has been used with varying success. In such materials, an interparticle spacing of the dispersoid of less than 2 microns is required for effective strengthening. It has also been shown that interparticle spacing in the dispersion-strengthened product decreases with decreasing particle size of both the oxide and the metal powders (ref. 1). However,

ultrafine powders (as small as a few hundredths of a micron) present difficulties because of the possibility of agglomeration, which may occur during handling, consolidation, or thermal processing.

To determine the presence and extent of such agglomeration, it has been necessary to prepare and examine consolidated and sintered specimens by replica electron microscopy. Recently, ultrafine powder blends were successfully consolidated by high-energy-rate compaction. These compacts are dense enough (without sintering) for direct replication and examination by electron microscopy (ref. 2). In this consolidated condition, it was not always possible to determine desired structural details, because of the cold work introduced during compaction. A low-temperature stress-relief annealing treatment preceding replication was used to improve details. Such an annealing treatment was not believed to cluster fine dispersoid particles (~ 0.01 to $0.05 \mu\text{m}$) appreciably, if at all; however, there remained some question as to whether any minute agglomeration would occur. Thus, a technique for examination of the completely unaltered (prior to compaction or sintering) powder blends was required.

A new technique using electron microscopy which permits discrimination between dispersoid and matrix particles in ultrafine metal-oxide powder blends is described herein. The technique clearly shows size, shape, and degree of agglomeration of oxide particles and similarly, but less clearly, characterizes the metal matrix particles. The ultrafine powder blends studied included the metals nickel, chromium, tungsten, and nichrome each blended with thoria or alumina; however, only a study of the compacts of nickel and tungsten with thoria and alumina as dispersoids is presented herein.

MATERIALS, APPARATUS, AND PROCEDURE

The materials that were studied with the electron-microscopy technique are given in table I. Powder blends of nickel - 4 volume percent thorium oxide and nickel - 4 volume percent aluminum oxide were prepared by ball milling. A powder blend of tungsten - 2 volume percent thorium oxide was prepared by vapor deposition.

TABLE I. - MATERIALS INVESTIGATED

Specimen	Matrix	Oxide additive	Method of blending
1	Tungsten	2 Percent thorium oxide (ThO_2)	Vapor deposition
2	Nickel	4 Percent thorium oxide (ThO_2)	Ball milling
3	Nickel	4 Percent aluminum oxide (Al_2O_3)	Ball milling

The procedure for preparing the powders for electron microscopic examination is as follows: About 30 milligrams of each powder blend are placed on a glass slide, and a few drops of Cellosolve (ethylene glycol monoethyl ether) are added. The diluted slurry is lightly dispersed with a spatula and spread over the glass slide. After drying, the film of dried slurry on the slide is shadowed with platinum at an angle of approximately 20°, after which a 0.02-micron thickness of carbon is deposited vertically. This film is then scored into 1/8-inch (0.31-cm) grid-size squares. The slide with the film scored in the form of small squares is immersed in acid or water to float off the carbon film containing the metal-oxide powders. When nickel is the matrix powder, the solutions used to separate the carbon films from the glass slides are also used to dissolve away the nickel from the film (see following table).

Matrix material	Solvent	Approximate time, hr	Remarks
Nickel	30 Percent nitric acid in water	24	Floated off directly in acid solution
Tungsten	2 Parts water 2 Parts nitric acid 1 Part hydrofluoric acid	24	Transferred to acid solution after separating film from glass slide in water

Water is used to float the film containing the tungsten and oxides, since hydrofluoric acid (HF), the acid to be used to dissolve tungsten, would attack the glass slide and contaminate the specimen. The water-floated films (grid-size squares) are then transferred to a solution of nitric acid and hydrofluoric acid to leach out the metal matrix. In both cases, the dissolution of the metal matrix is completed after 24 hours. Slow dissolution is necessary to avoid a shifting of the dispersoid. The carbon films containing the undissolved dispersoid are then washed three to four times in distilled water, placed on an electron-microscope grid, dried on filter paper, and examined in the electron microscope. Electron micrographs are made of the carbon film containing only the dispersoid at magnifications up to 75 000.

DISCUSSION AND RESULTS

The preparation procedure described may be termed a "shell" technique. Electron micrographs obtained with this technique were compared with micrographs obtained by placing the same starting powder materials directly on the electron-microscope grid. For comparison of the results of the shell method and those obtained from consolidated

and sintered blends, the same blends were also prepared by using a cartridge-actuated compaction press and then annealing (ref. 2) to reveal structures more clearly. Two of these specimens were annealed at a low temperature of 1700^o F (927^o C) for 1 hour, and after examination by replication were given an additional 1-hour anneal at 2300^o F (1260^o C) and examined again. The third specimen was sintered at 2000^o F (1093^o C) in hydrogen for 2 hours and annealed at 2000^o F (1093^o C) in vacuum for 6 hours.

The following discussion is a comparison of the results obtained from the shell method with those obtained by consolidation and sintering.

An electron micrograph of a powder blend of tungsten and 2 volume percent oxide placed directly on a carbon support film that had been positioned previously on an electron-microscope grid is shown in figure 1(a). If one assumes that the large, dense-looking (black) particles are those of the tungsten (high percentage) and that the small particles are those of the thoria (small percentage), an indirect indication as to how many particles of the tungsten or the thoria there are may be obtained. This assumption may not be valid, since small particles in the tungsten powder and large ones in the thoria powder might have been present. Also, some dispersoid may be invisible because of its location in front of or behind matrix particles or within clusters of them. This kind of examination may be considered adequate for the determination of particle sizes of the blend but cannot be relied upon for the identification of the individual sizes of the components.

Figure 1(b) shows the thoria dispersoid in a film unobstructed by the presence of the tungsten, which here has been dissolved away by the shell method. In most instances the thoria (black) is located around the tungsten-powder particle shell (actually a carbon replica of tungsten particles present prior to the acid leaching). In some cases, the thoria appears to be present within the area of the former tungsten particle (shadowed zone indicated by an arrow). In other cases, the oxides are present in small clusters.

Figure 1(c) illustrates the tungsten-thoria blend after compaction and a stress-relief anneal (1 hr at 1700^o F or 927^o C). After this low (for tungsten) sintering temperature, a coarsening of the dispersoid (arrow) and a concentration of dispersoids in the prior powder particle boundaries occurs. Only a limited number of dispersoid particles are detected within the matrix particles.

Figure 1(d) shows the same compacted and sintered blend as figure 1(c), but in this case the material received an additional 1-hour sintering at 2300^o F (1260^o C). At this temperature, most of the thoria agglomerated to coarse particles. In figure 1(b), the source of the agglomeration can be deduced from the observation that most of the thoria particles are not discretely dispersed but touch one another or are separated by only a very short distance. Thus when heated, they apparently agglomerated or sintered together.

The same interpretations apply to the nickel-thoria powder blends of figure 2. The thoria dispersoid (fig. 2(a)) is coarsened and shows evidence of slight localized flocculations. The resulting compacted and sintered structure (fig. 2(b)) correspondingly also shows large dispersoid sizes, which again are believed to result from sintering. Those particles that appear discrete and small in figure 2(b) (arrow) are comparable in size to those in the shell preparation of figure 2(a) (arrow). They were sufficiently far from other dispersoid particles or groups of particles not to coarsen during sintering.

In figures 3(a) and (b) (the nickel-alumina shell preparation and compaction-sinter replica, respectively) a very good oxide dispersion with a predominant particle size of about 0.008 to 0.015 micron is evident. The alumina particles (fig. 3(a) (arrow)) are lighter in appearance than the thoria particles in figure 2(a), a result of the lower opacity to the electron beam of alumina relative to thoria. Clustering of the dispersoid can be seen; however, the largest clusters are all below 0.1 micron. The structure of the compacted and sintered blend again corresponds to the unaltered powder (shell preparation) by having a predominance of dispersoid particles smaller than 0.1 micron.

Chromium and nichrome specimens were prepared, but photomicrographs are not presented. The results were essentially the same as those for the nickel- and tungsten-base materials.

SUMMARY OF RESULTS

An electron-microscope technique was developed for use with dispersion-strengthened materials for the purpose of obtaining better control of the microstructure. The significant results of using this technique are as follows:

1. The specimen-preparation technique permits the differentiation between oxide and metal particles in an unconsolidated powder blend.

2. The technique produces a carbon film supported on an electron-microscope grid in which particles of the powder blend are suspended, and from which the metallic or matrix particles have been selectively leached, leaving the oxide dispersoid particles undisturbed.

3. The technique permits the visual determination of the size, shape, and degree of agglomeration of the metal and dispersoid particles prior to consolidation or sintering.

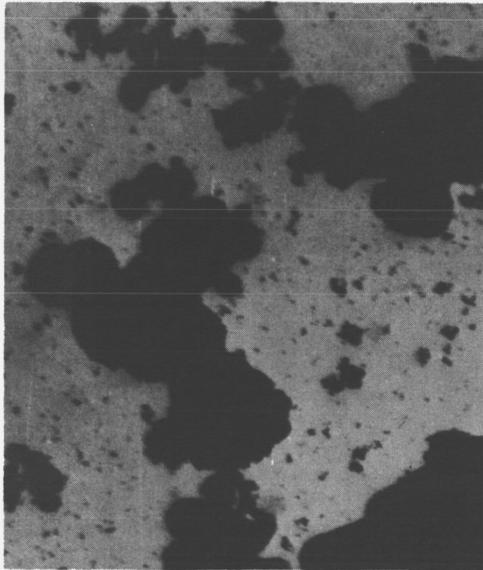
4. The powder distributions observed by the method used in this study persist through compacting and sintering steps into the final product. Thus, if the oxide particles are suitably dispersed in the original powder blend, the dispersoid can remain as fine, well-distributed particles in the final dispersion-strengthened product. In the same way, if large-sized clusters consisting of fine particles are present in the powder

blend, large particles of the same general size as the clusters will be observed in the sintered product.

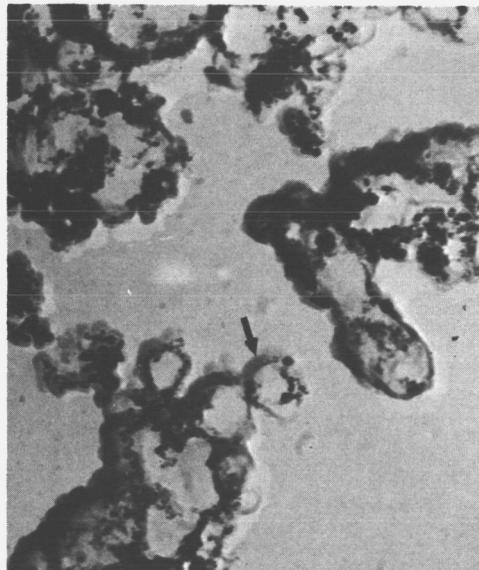
Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, July 24, 1967,
129-03-01-05-22.

REFERENCES

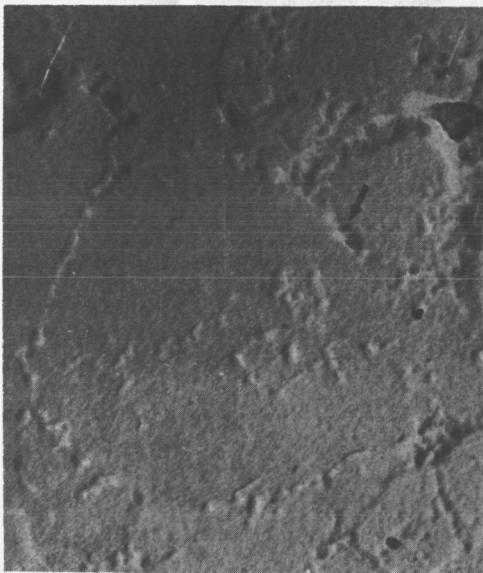
1. Cremens, Walter S.: Use of Submicron Metal and Nonmetal Powders for Dispersion-Strengthened Alloys. *Ultrafine Particles*. W. E. Kuhn, ed., John Wiley & Sons, Inc., 1963, pp. 457-478.
2. Reinhardt, Gustav; Cremens, Walter S.; and Weeton, John W.: Cold Consolidation of Metal Plus Dispersoid Blends for Examination by Electron Microscopy. NASA TN D-3511, 1966.



(a) Powder dispersion. X28 300.



(b) Shell. X75 000.

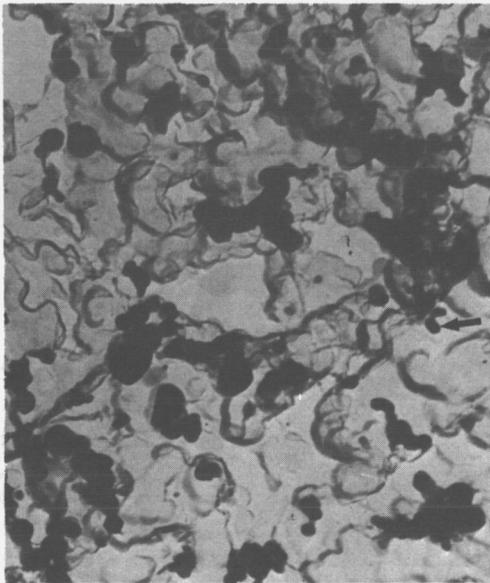


(c) Compacted and sintered for 1 hour at 1700° F (927° C). X75 000.

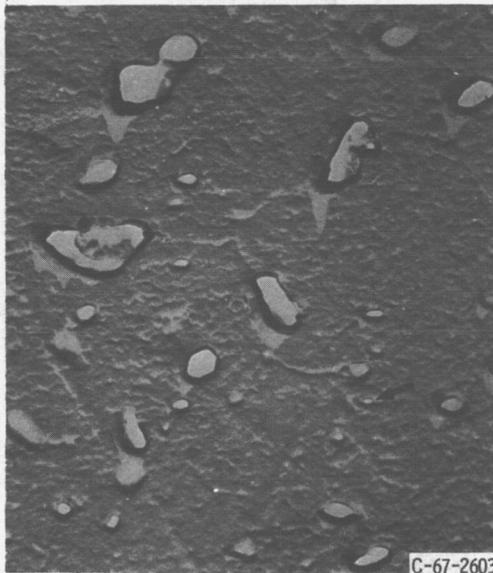


(d) Compacted and sintered for 1 hour at 1700° F (927° C) and 1 hour at 2300° F (1260° C). X27 000.

Figure 1. - Vapor-deposited tungsten plus 2 volume percent thoria.

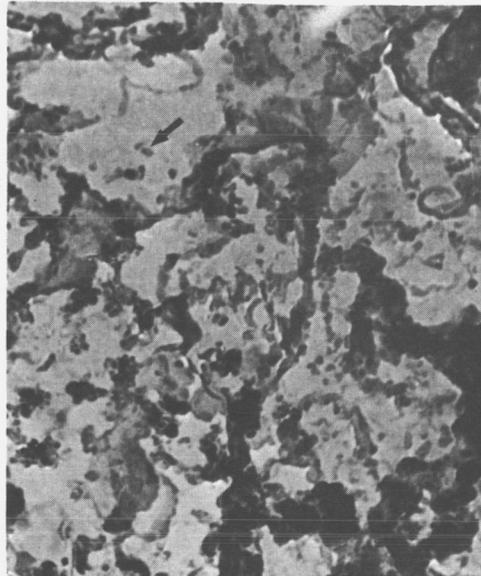


(a) As-blended; shell. X49 000.

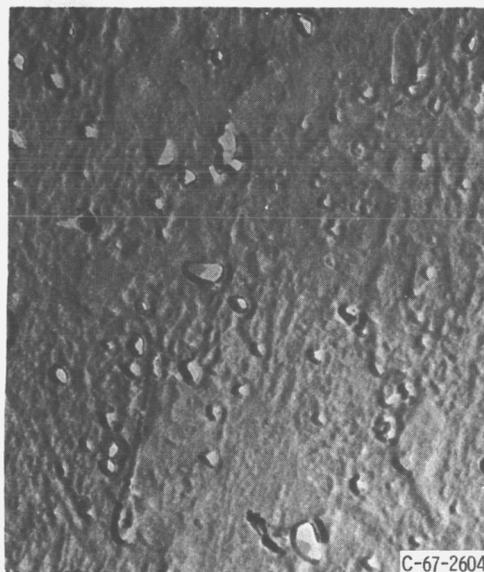


(b) Compacted and sintered for 2 hours at 2300° F (1260° C) in hydrogen. X27 000.

Figure 2. - Ball-milled nickel plus 4 volume percent thoria.



(a) As-blended; shell. X75 000.



(b) Compacted and sintered for 2 hours at 2000° F (1093° C) in hydrogen and annealed 6 hours at 2000° F (1093° C) in vacuum. X27 000.

Figure 3. - Ball-milled nickel plus 4 volume percent alumina.